Complex formation of $^{159/160}Tb^{3+}$ with glycolate and gluconate in inert electrolytes

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Stability constants for complexation of divalent and trivalent metal ions with organic ligands such as α-hydroxycarboxylic acid are highly essential to investigate solubility, sorption and migration of radionuclides in near and far fields of radioactive waste disposal.

Complex formation equilibria of Tb^{3+} with glycolate and gluconate ligands in neutral aqueous electrolytes (pH = 7) at T = 298.1 K were investigated by means of electromigration measurements of non-carrier-free $^{159/160}Tb^{3+}$.

^{160}Tb ($T_{1/2}$ = 72.3 d) was produced by neutron irradiation of terbium oxide at the BER II reactor (HMI, Berlin). Terbium solutions for electro-migration measurements were prepared by evaporation of about 200 µL of a $^{159/160}Tb^{3+}$ - stock solution and dissolution of the residue with 100 µL of $Na(H)ClO_4$, pH = 4.

Aqueous solutions of type $NaClO_4$/NaOH/HL with an overall ionic strength µ = 0.1 and a pH around 7 were used for the investigations, L = glycolate and gluconate respectively. The pH of the electrolytes was measured by means of glass electrodes calibrated by standard buffer solutions.

The volume of the $^{159/160}Tb^{3+}$ solution injected into the electrolyte in the electromigration tube was about 1-2 µL corresponding to a metal amount in the migration zone of ≈ 10^{-7} mol. Measurements of ion mobilities were performed with an electric field intensity of 10 V/cm.

As an example, experimental results obtained for $^{159/160}Tb^{3+}$ electromigration in gluconate electrolytes are illustrated in Fig.1.

The quantitative treatment of the complex formation results was based on the following mechanism:

$$Tb^{3+} + nL^- \longleftrightarrow^{\beta_n} TbL_n^{3-n} \quad (1)$$

where β_n are the stoichiometric overall complex formation constants. Application of the general electromigration equation for n=1,2,3 for the variation of the overall ion mobility, u, with the ligand concentration leads to:

$$u = \frac{u^o_{Tb^{3+}} + u^o_{TbL^{2+}} \cdot K_1 \cdot [L^-] + u^o_{TbL_2^+} \cdot K_1 \cdot K_2 \cdot [L^-]^2}{1 + K_1 \cdot [L^-] + K_1 \cdot K_2 \cdot [L^-]^2 + K_1 \cdot K_2 \cdot K_3 \cdot [L^-]^3} \quad (2)$$

with u_i^o the individual ion mobility of the species acting in the equilibrium and K_n the stepwise stochiometric complex formation constants. The values of K_n and u_i^o obtained from the fit of the experimental data with Eq.(2) are listed in Table 1 and Table 2 respectively.

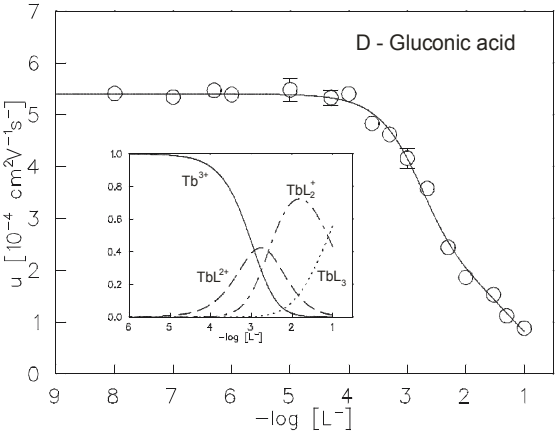

Fig.1. Overall ion mobilities of $^{159/160}Tb^{3+}$ vs. gluconate ligand concentration. $NaClO_4$/NaOH/HL electrolytes, µ = 0.1, pH 6.90-7.16, T = 298.1 K. The window in the diagram displays the relative distribution of the species calculated with the experimental K_n-values (Tab.1).

Table 1. Stepwise complex formation constants for the complexation of terbium with glycolate and gluconate ligands.µ = 0.1, pH = 7, T = 298.1 K. a) µ = 0.2.

	$logK_1$	$logK_2$	$LogK_3$
Glycolate	2.67(9)	1.71(10)	1.11(9)
Lit.[2] →	*2.82*	*2.09*	*1.12*
Gluconate	2.93(10)	2.58(10)	1.11(9)
Lit.[2] →	*2.47* [a)]	*2.20* [a)]	-

Table 2. individual ion mobility (10^{-4} cm^2/Vs) of the species for the complex formation of terbium with glycolate and glucanate ligands. µ = 0.1, T = 298.1 K.

	$u^o_{Tb^{3+}}$	$u^o_{TbL^{2+}}$	$u^o_{TbL_{+2}}$
Glycolate	5.63(16)	3.79(13)	1.85(13)
Gluconate	5.40(6)	3.60(10)	1.80(10)

Gluconic acid forms stronger complexes with terbium as glycolic acid. The same was also observed for samarium from batch experiments [1]. The next studies will deal with the complexation of terbium and cobalt ions with iso-sacharic acid.

[1] G. Getahun et al., Institut für Kernchemie, Uni. Mainz, Jahresbericht 2000, C4. [2] Critical Stability Constants, Vol.3, A. E. Martell, R. M. Smith, Plenum Press New York and London (1997).